GAS – LIQUID CHROMATOGRAPHY – MASS SPECTROMETRY OF THE ACETATES OF PARTIALLY METHYLATED METHYL GLYCOSIDES

V. 6-DEOXYHEXOSES

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In preceding papers we have reported the results of a study of the mass spectra of acetates of partially methylated methyl hexo- and pentopyranosides. The characteristic nature of the mass spectra made it possible to determine the pattern of methylation, and from the T values it was possible to identify the stereoisomers, i.e., to distinguish a methyl ether of the mannose series from that of the glucose series with the same methylation pattern. The present paper gives information on the mass spectra of acetates of partially methylated Me α-L-Fuc, Me α-L-Rha, and Me β-L-Fuc, the relative retention times (T)* of which are given below.

Initial methyl ethers of methyl glycosides	T	Initial methyl ethers of methyl glycosides	T
2,3-OMe$_2$-α-Fuc	1.93	3-OMe$_1$-β-Fuc	4.40
3,4-OMe$_2$-α-Fuc	2.38	2-OMe$_1$-β-Fuc	3.67
2,4-OMe$_2$-α-Fuc	2.84	2,3-OMe$_2$-α-Rha	2.27
3-OMe$_1$-α-Fuc	3.30	3,4-OMe$_2$-α-Rha	0.65
4-OMe$_1$-α-Fuc	3,85	2,4-OMe$_2$-α-Rha	1,85
2-OMe$_1$-α-Fuc	4,03	3-OMe$_1$-α-Rha	2,87
α-Fuc	4,63	4-OMe$_1$-α-Rha	3,05
2,3-OMe$_2$-β-Fuc	1.79	2-OMe$_1$-α-Rha	3.61
2,4-OMe$_2$-β-Fuc	2.34	α-Rha	4.20

The spectra of permethylated Me β-L-Fuc (I) and of the acetates of Me 2,3-OMe$_2$-β,L-Fuc (II), Me 2,4-OMe$_2$-α,L-Fuc (III), Me 3,4-OMe$_2$-α, L-Rha (IV), Me 2-OMe-β, L-Fuc (V), Me-3-OMe-β,L-Fuc (VI), Me 4-OMe-α,L-Rha (VII) and Me α,L-Fuc (VIII) are given in Table 1. On drawing an analogy between the mass spectra of the dimethyl ethers (II, III, and IV) and the spectrum of Me 2,3,4-OMe$_3$-β-L-Fuc (I) the peaks of one and the same series of ions can be detected [1]. Depending on the position of the OAc groups, the relative intensities and mass numbers of the ions will change. These changes permit an unambiguous determination of the positions of the methoxy groups from the mass spectra of the methyl 6-deoxyhexopyranosides.

In the mass spectrum of (II) with a 2,3-OMe$_2$ fragment of the structure, the main peak with m/e 88 is due to the ion H_1^2, as in the spectrum of (I). Because of the OMe substituents at C-1,2,3, only in the spectrum of (II) does the peak of an ion with m/e 119 appear, since its formation presupposes the migration of OMe, but not OAc, from C-3 to C-1, and the preceding cleavage of C-1–C-2 is more probable between atoms bearing OMe groups.

Although in the spectrum of (IV) (3,4-OMe$_2$) the peak with m/e 88 is the main peak, its intensity is lower than in the spectrum of (II). Furthermore, the spectrum of (IV) has a considerable peak with m/e 72 of the ion K_1.

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*T = 0 is the retention time of the full acetate of hydroxylamine, T = 10 is the retention time of the full acetate of D-galactononitrile; 3% of NPGS, Aeropak 30, 60-80 mesh, 6 mm × 1.5 m, 125-225°C, 5°C/min, FI detector, Pye Unicam chromatograph.

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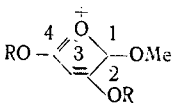
TABLE 1. Mass Spectra of Acetates of Methylated Methyl 6-Deoxyhexopyranosides

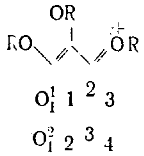
m/e	I	II	III	IV	V	VI	VII	VIII
43	10	36	70	67	>100	>100	>100	>100
45	21	14	2,5	23	6	11	15	5
57	—	—	—	9	—	—	—	8
59	—	5,0	1,5	13	2,6	17	24	9
61	—	0,7	—	—	0,8	4	—	
71	5	—	12	—	5	7	14	27
72	19	—	54	41	..,6	13	90	4
73	25	16	16	—		—	—	4
74	—	9,0	100	58	100	100	100	27
75	39	50	61	59	4	53		—
83	—	—	—	20	10	9	11	25
85	—	23	21	20,5	19	47	10	4
87	—	6,0	10	—	12	11	70	21
88	100	100	58	100	5,0	7	6	--
96	—	—	—	—	5,0	—	5	7,5
97	—	10	16	—	2,6	—	—	—
99	—	1,6	—	5,3	2,4	4	17	12
100	—	1,4	—	—	1,8	11	—	32
101	24	8,8	72	19,0	1,8	14	4	17,5
102	—	—	6,0	—	—	—	10	28
103	—	1,8	—	4,0	4,7	—	7	22
111	—	—	5,0	3,0	—	—	6	16
113	—	1,7	—		10,5	9	13	33
114	—	2,6	—	3,0	10	6	8	—
115	—	4,3	—	4,0	12,1	8	11	27
116	—	3,6	73	23	26,3	44	32	12
117	—	1,4	10	—	—	—	—	—
119	4,0	1,1	—	—	—	—	—	—
125	—	1,0	5,0	1,5	1,3	1,3	—	3
127	—	—	—	—	—	0,6	—	3
129	8,0	4,6	40	9,0	10,5	7,0	85	8
131	4	0,5	—	—	—	—	—	—
140	—	—	—	—	—	—	—	8
141	—	—	—	1,0	0,35	0,7	—	—
142	—	—	—	—	0,3	1,2	5	21
143	—	0,4	3,4	3,3	0,6	1,6	3,7	7
144	—	—	—	3,0	—	0,6	3,3	36
145	—	—	2,4	3,0	—	—	—	12
153	—	—	—	—	—	0,4	—	1,0
156	—	0,5	—	1,0	3,5	1,0	5,7	—
157	1,0	0,4	12	1,0	3,0	1,6	2,7	48
159	—	—	—	1,3	—	1,0	—	—
171	—	—	—	—	—	—	—	4,2
172	—	—	—	—	0,8	—	2,7	—
173	—	0,1	0,4	—	0,35	7	2,3	—
176	4,0	—	—	—	—	—	—	—
184	—	—	—	—	—	0,4	5,3	18,3
185	—	0,5	0,6	6,0	0,1	1,1	6,7	1,0
188	—	—	0,3	—	—	—	—	—
189	0,5	—	0,2	—	0,44	—	2,3	—
200	—	—	—	—	—	—	—	1,7
201	—	—	—	0,01	—	—	—	1,45
202	—	—	—	—	—	0,3	—	—
204	—	2,9	0,4	7,0	—	—	0,5	--
213	—	—	—	—	—	0,1	-	1,5
216	—	—	—	—	0,04	0,2	—	—
217	—	0,5	1,0	3,3	0,04	—	—	0,8
232						0,4		
233						0,1		
243								
244								0,8
245					1,0	0,4	1,7	
247		0,06	0,06					
273								5
275					0,06	0,1		

The spectrum of (III) (2,4-OMe$_2$) is distinguished by considerable peaks of ions of series G. In the region of high mass numbers the spectrum is characterized by a peak with m/e 157 of the C_2 and A_2 ions and by peaks of lower intensity at 188 and 189 of the C_p and C ions. The main direction of the decomposition of Me 2-OMe-β-L-Fuc (V) predicates the cleavage of the C_1-C_2 bond, which leads to strong H ions with m/e 116 and 74, and to C (B in Biemann's nomenclature) ions with m/e 156, 157, 114, 115, and 97, 96.

The introduction of an OMe group at C-3 is responsible for a strong peak with m/e 75 of the J_1^1 ion in the spectrum of (VI). Since an OMe group is more stable than an OAc group, the spectrum of (VI) shows peak B_1 with m/e 232 and O_1^1 with m/e 159. The spectra of the 2- and 4-OMe ethers (V and VIII) show only the peak of the ion B_2 (B_1−HOAc) with m/e 172. A peak with m/e 189 in the spectra of these two compounds is due to an ion with the possible structure E_f. The formation of E_f presupposes the presence of a labile substituent at C_3 (OAc, for example). In fact, in the spectrum of the 3-OMe derivative (VI) this peak is absent, and in the spectrum of the full acetate of Me α-L-Fuc (V) it is shifted to m/e 217.



E_f



Among the monomethyl ethers, the spectrum of (VII) (4-OMe) is distinguished by an appreciable peak with m/e 72 of the K_1 ion and peaks with m/e 87 and 129 of G ions. Furthermore, the C_{2p} and C_2 ions are responsible for peaks with m/e 184 and, in part, m/e 185, i.e., they do not include OMe from the C_4 atom. The same peaks appear in the spectrum of the full acetate (VIII), although here they can be caused in part by the ions M − 2 × AcOH and M − (AcOH + AcO). A similar pattern has been observed in the spectra of the pentosides and hexosides, i.e., the loss of the C_4 substituent is specific for the 4-OMe ethers of methyl glycosides.

Assignment to a particular stereoisomer is made on the basis of T values.

SUMMARY

GLC−MS results have been obtained for acetates of partially methylated methyl 6-deoxyhexopyranosides that permit the positions of the OMe groups to be determined unambiguously and assignment to a definite stereoisomer to be made by means of T values.

LITERATURE CITED

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